VERIFICATION OF TRANSLATION

I, Hirozumi Ono, being a citizen of Japan, residing at c/o ASAHINA & CO., NS Bldg., No. 2-22, Tanimachi 2-chome, Chuo-ku, Osaka-shi, Osaka, 540-0012, Japan, do solemnly and sincerely declare as follows:

I am a translator, of ASAHINA & CO., of NS Bldg., No. 2-22, Tanimachi 2-chome, Chuo-ku, Osaka, 540-0012, Japan.

I am well acquainted with the English and Japanese languages.

The attached translation is a true and correct translation into the English language of Japanese Patent Application No. 2004-250242 filed on August 30, 2004.

I declare further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

This 10th day of August, 2010

by Hirozumi Ono

Hirozumi Ono

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[Material Name]	Claims	1
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[Document name] CLAIMS

1. A thermoplastic polymer composition, comprising a fluororesin (A) and a non-fluorine-containing cured rubber (B), wherein the fluororesin (A) comprises a fluorine-containing ethylenic polymer (a), and the non-fluorine-containing cured rubber (B) is at least one rubber (b) which is at least partially crosslinked.

2. The thermoplastic polymer composition of Claim 1, wherein the fluorine-containing ethylenic polymer (a) has a melting point of 120 to 310°C.

3. The thermoplastic polymer composition of Claim 1 or 2, wherein the rubber (b) is at least one rubber selected from the group consisting of an olefin rubber, an acrylic rubber, a nitrile rubber, a silicone rubber, a urethane rubber and an epichlorohydrin rubber.

4. The thermoplastic polymer composition of Claim 1, 2 or 3, wherein the cured rubber (B) is a rubber, in which the rubber (b) is dynamically-vulcanized in the presence of the fluororesin (A) and a crosslinking agent (C).

5. The thermoplastic polymer composition of Claim 1, 2, 3 or 4, wherein the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase in the structure of the composition.

6. The thermoplastic polymer composition of Claim 1, 2, 3,

4 or 5, wherein the fluororesin (A) is a copolymer of tetrafluoroethylene and ethylene.

7. The thermoplastic polymer composition of Claim 1, 2, 3, 4 or 5, wherein the fluororesin (A) is a copolymer of tetrafluoroethylene and a perfluoro ethylenically unsaturated compound represented by the following general formula (1):

$$CF_2=CF-R_f^1 \qquad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms).

8. The thermoplastic polymer composition of Claim 1, 2, 3, 4 or 5, wherein the fluororesin (A) is a copolymer comprising 19 to 90 % by mole of a tetrafluoroethylene unit, 9 to 80 % by mole of an ethylene unit, and 1 to 72 % by mole of a perfluoro ethylenically unsaturated compound unit represented by the following general formula (1):

$$CF_2=CF-R_f^1 \qquad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms).

9. The thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 6, 7 or 8, wherein the fluororesin (A) is polyvinylidene fluoride.

10. The thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 6, 7, 8 or 9, wherein the rubber (b) is at least one selected from the group consisting of an ethylene-propylene-diene rubber, an ethylene-propylene rubber, a butyl rubber, a halogenated butyl rubber, an acrylonitrile-butadiene rubber, a hydrogenated acrylonitrile-butadiene rubber, a dimethylsilicone rubber, a vinylmethylsilicone rubber and a styrene-diene-styrene block copolymer.

11. The thermoplastic polymer composition of Claim 4, 5, 6, 7, 8, 9 or 10, wherein the crosslinking agent (C) is at least one selected from the group consisting of organic peroxide, an amine compound, a hydroxy compound, a phenol resin compound, a sulfur compound, a bismaleimide compound and a quinoid compound.

12. The thermoplastic polymer composition of Claim 4, 5, 6, 7, 8, 9, 10 or 11, wherein the rubber (b) has at least one crosslinkable functional group in its molecule, and the crosslinking agent (C) is a compound having two or more functional groups and being capable of reacting with said functional group.

13. A molded article, comprising the thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 7, 8, 9, 10 11 or 12.

14. A sheet, comprising the thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 7, 8, 9, 10, 11 or 12.

15. A film, comprising the thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 7, 8, 9, 10, 11 or 12.

16. A laminate, which has layers comprising the thermoplastic polymer composition of Claim 1, 2, 3, 4, 5, 7, 8, 9, 10, 11 or 12.

[Document Name] SPECIFICATION

[Title of the Invention]

THERMOPLASTIC POLYMER COMPOSITION

[Technical Field]

【0001】

The present invention relates to a thermoplastic polymer composition comprising a specific fluororesin and a specific cured rubber, and a molded article, a sheet, a film or a laminate, which comprises the thermoplastic polymer composition.

[Prior Art]

【0002】

Since cured rubbers have excellent heat resistance, chemical resistance and flexibility, they are widely used in automobile parts, consumer electric appliance parts, electric wire covering, parts for medical use. However, in order to produce molded articles using cured rubbers, it is general to carry out several complicated steps, for example, (1) a step of mixing an uncured rubber with a crosslinking agent, an acid accepter, a filler, (2) a step of molding by using an extruder or an injection molding machine, and (3) a step of crosslinking by using a press or an oven, so it takes a long time to obtain a molded article. In addition, there is a problem such that rubbers do not melt after being crosslinked, and thus the rubbers can not be subjected to post-process such as melt-adhesion and cannot be re-used.

【0003】

In order to solve the above-described problem, so called

dynamic vulcanization technique has been developed such that crosslinking is conducted while melt-kneading a thermoplastic resin such as polypropylene resin, an uncrosslinked crosslinkable rubber and a crosslinking agent all together in an extruder.

【0004】

As a dynamically-vulcanized rubber (TPV), for example, one having a structure in which a crosslinked ethylene-propylene-diene rubber (EPDM) is dispersed in a propylene resin (see, e.g., Patent Documents 1, 2 and 3) is widely studied and practically used in a part.

【0005】

However, it is a fact that since a matrix of the above-mentioned TPV comprising a polypropylene resin and a crosslinked EPDM is a polypropylene resin, the TPV does not have heat resistance at a melting point of a polypropylene resin or more, and chemical resistance is also inferior.

【0006】

For the purpose of developing TPV excellent in heat resistance and chemical resistance, it is known TPV having a structure that a polyester resin or 4-methyl-1-pentene resin is used as a matrix and a cured rubber is dispersed therein (see, e.g., Patent Documents 4 and 5). However, compared with TPV comprising a polypropylene resin and crosslinked EPDM, heat resistance and chemical resistance of these TPV are somewhat improved, but are not sufficient, and there is a problem that flexibility and mechanical performance are inferior.

【0007】

Further, there is studied TPV having a structure that a

fluororesin is used as a matrix and a crosslinked fluororubber is dispersed therein as a cured rubber (see, e.g., Patent Documents 6, 7 and 8). Although such TPV has excellent heat resistance and chemical resistance due to a matrix of fluororesin, they have poor low-temperature property, poor flexibility and poor performance as to compression set, and do not have enough mold-processability.

【0008】

[Patent Document 1] JP-A-6-287368

[Patent Document 2] JP-A-6-256571

[Patent Document 3] JP-A-11-228750

[Patent Document 4] JP-A-10-212392

[Patent Document 5] JP-A-11-269330

[Patent Document 6] JP-A-61-57641,

[Patent Document 7]JP-A-5-140401

[Patent Document 8] JP-A-6-228397

[Disclosure of Invention]

[Problem to be Solved by the Invention]

【0009】

An object of the present invention is to provide a thermoplastic polymer composition which has both excellent heat resistance and chemical resistance, and also has flexibility and excellent mold-processability.

[Means to Solve the Problem]

【0010】

Namely, the present invention relates to a thermoplastic polymer composition, comprising a fluororesin (A) and a non-fluorine-containing cured rubber (B), wherein the fluororesin (A)

comprises a fluorine-containing ethylenic polymer (a), and the non-fluorine-containing cured rubber (B) is at least one rubber (b) which is at least partially crosslinked.

【0011】

It is preferable that the fluorine-containing ethylenic polymer (a) has a melting point of 120 to 310°C.

【0012】

It is preferable that the rubber (b) is at least one rubber selected from the group consisting of an olefin rubber, an acrylic rubber, a nitrile rubber, a silicone rubber, a urethane rubber and an epichlorohydrin rubber.

【0013】

It is preferable that the cured rubber (B) is a rubber in which the rubber (b) is dynamically vulcanized in the presence of the fluororesin (A) and a crosslinking agent (C).

【0014】

It is preferable that the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase in the structure of the composition.

【0015】

It is preferable that the fluororesin (A) is a copolymer of tetrafluoroethylene and ethylene.

【0016】

It is preferable that the fluororesin (A) is a copolymer of tetrafluoroethylene and a perfluoro ethylenically unsaturated compound represented by the following general formula (1):

$$CF_2=CF-R_f^1 \quad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms).

【0017】

It is preferable that the fluororesin (A) is a copolymer comprising 19 to 90 % by mole of a tetrafluoroethylene unit, 9 to 80 % by mole of an ethylene unit, and 1 to 72 % by mole of a perfluoro ethylenically unsaturated compound unit represented by the following general formula (1):

$$CF_2=CF-R_f^1 \quad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms).

【0018】

It is preferable that the fluororesin (A) is polyvinylidene fluoride.

【0019】

It is preferable that the rubber (b) is at least one selected from the group consisting of an ethylene-propylene-diene rubber, an ethylene-propylene rubber, a butyl rubber, a halogenated butyl rubber, an acrylonitrile-butadiene rubber, a hydrogenated acrylonitrile-butadiene rubber, a dimethylsilicone rubber, a vinylmethylsilicone rubber and a styrene-diene-styrene block copolymer.

【0020】

It is preferable that the crosslinking agent (C) is at least one selected from the group consisting of organic peroxide, an amine compound, a hydroxy compound, a phenol resin compound, a sulfur compound, a bismaleimide compound and a quinoid compound.

【0021】

It is preferable that the rubber (b) has at least one crosslinkable functional group in a molecule, and the crosslinking agent (C) is a compound having two or more functional groups and being capable of reacting with the above-mentioned functional group.

【0022】

The present invention relates to a molded article, a sheet, or a film comprising the thermoplastic polymer composition.

【0023】

The present invention relates to a laminate, which has layers comprising the thermoplastic polymer composition.

[Effect of the Invention]

【0024】

In the thermoplastic polymer composition of the present invention, cured rubber particles are dispersed in a fluorine-containing ethylenic polymer, therefore the thermoplastic polymer composition has both excellent heat resistance and chemical resistance, and also has flexibility and excellent mold-processability.

[Best Mode for Carrying Out the Invention]

【0025】

The present invention relates to a thermoplastic polymer composition comprising the fluororesin (A) and the non-fluorine-containing cured rubber (B), wherein the fluororesin (A)

comprises a fluorine-containing ethylenic polymer (a), and the non-fluorine-containing cured rubber (B) is at least one kind of rubber (b) which is at least partially crosslinked.

【0026】

A melting point of the fluororesin (A) is 120 to 310°C, more preferably 150 to 290°C, and further more preferably 170 to 250°C. When the melting point of fluororesin (A) is less than 120°C, heat resistance of the obtained thermoplastic polymer composition tends to be lowered, and when it is more than 310°C, in the case of dynamically vulcanizing the rubber (b) in the presence of the fluororesin (A) and crosslinking agent (C) under a melting condition, a melting temperature is required to be higher than the melting point of the fluororesin (A), however, the rubber (b) tends to be thermally deteriorated in this case.

【0027】

The fluororesin (A) is not particularly limited, but may be a polymer containing at least one kind of fluorine-containing ethylenic polymer (a). As an ethylenically unsaturated compound composing the fluorine-containing ethylenic polymer (a), examples are perfluoroolefins such as tetrafluoroethylene and perfluoro ethylenically unsaturated compound represented by the general formula (1):

$$CF_2=CF\text{-}R_f^1 \qquad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms); and fluoroolefins such as chlorotrifluoroethylene, trifluoroethylene, hexafluoroisobutene,

vinylidene fluoride, vinyl fluoride, ethylene chloride trifluoride, and a compound represented by the general formula (2):

$$CH_2=CX^1(CF_2)_nX^2 \quad (2)$$

(wherein X^1 represents hydrogen atom or fluorine atom, X^2 represents hydrogen atom, fluorine atom, or chlorine atom, and n represents an integer of 1 to 10).

【0028】

Also, as an ethylenically unsaturated compound composing fluorine-containing ethylenic polymer (a), non-fluorine-containing ethylenically unsaturated compounds other than the above-described fluoroolefin and perfluoroolefin can be listed. Examples of the non-fluorine-containing ethylenically unsaturated compound are ethylene, propylene, or alkyl vinyl ethers. Herein, the alkyl vinyl ether indicates an alkyl vinyl ether having an alkyl group with 1 to 5 carbon atoms.

【0029】

Among them, from the viewpoint that heat resistance and oil resistance of the obtained thermoplastic polymer composition are excellent, and a molding process is easy, a fluorine-containing ethylenic polymer (a) comprising tetrafluoroethylene and ethylene is preferable, and a fluorine-containing ethylenic polymer (a) comprising 20 to 80 % by mole of a tetrafluoroethylene unit and 80 to 20 % by mole of an ethylene unit is more preferable. Also, the fluorine-containing ethylenic polymer (a) comprising tetrafluoroethylene and ethylene may contain the third component,

and an example of the third component is 2,3,3,4,4,5,5-heptafluoro-1-pentene ($CH_2=CFCF_2CF_2CF_2H$).

【0030】

An amount of the third component is preferably 0.1 to 3 % by mole based on the fluorine-containing ethylenic polymer (a).

【0031】

Also, from the viewpoint that heat resistance and oil resistance of the obtained thermoplastic polymer composition are excellent, and a molding process is easy, the fluorine-containing ethylenic polymer (a) is preferably one comprising tetrafluoroethylene and a perfluoro ethylenically unsaturated compound represented by the general formula (1):

$$CF_2=CF\text{-}R_f^1 \qquad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms). The fluorine-containing ethylenic polymer (a) comprising 90 to 99 % by mole of a tetrafluoroethylene unit and 1 to 10 % by mole of a perfluoro ethylenically unsaturated compound unit represented by the general formula (1) is more preferable. Also, the fluorine-containing ethylenic polymer (a) comprising tetrafluoroethylene and a perfluoro ethylenically unsaturated compound represented by the general formula (1) may contain the third component.

【0032】

Also, from the viewpoint that heat resistance and oil resistance of the thermoplastic polymer composition are excellent, and

a molding process is easy, the fluorine-containing ethylenic polymer (a) is preferably one comprising tetrafluoroethylene, ethylene and a perfluoro ethylenically unsaturated compound represented by the general formula (1):

$$CF_2{=}CF\text{-}R_f^1 \qquad (1)$$

(wherein R_f^1 represents $-CF_3$ or $-OR_f^2$, and R_f^2 represents a perfluoroalkyl group having 1 to 5 carbon atoms). The fluorine-containing ethylenic polymer (a) comprising 19 to 90 % by mole of a tetrafluoroethylene unit, 9 to 80 % by mole of an ethylene unit, and 1 to 72 % by mole of a perfluoro ethylenically unsaturated compound unit represented by the general formula (1) is more preferable, and the fluorine-containing ethylenic polymer (a) comprising 20 to 70 % by mole of a tetrafluoroethylene unit, 20 to 60 % by mole of an ethylene unit, and 1 to 60 % by mole of a perfluoro ethylenically unsaturated compound unit represented by the general formula (1) is further more preferable.

【0033】

The fluorine-containing ethylenic polymer (a) comprising tetrafluoroethylene, ethylene and a perfluoro ethylenically unsaturated compound represented by the general formula (1) may contain an additional component, and an example of the additional component can be 2,3,3,4,4,5,5-heptafluoro-1-pentene ($CH_2{=}CFCF_2CF_2CF_2H$).

【0034】

An amount of the additional component is preferably 0.1 to 3 % by mole based on the fluorine-containing ethylenic polymer (a).

【0035】

Further, from the viewpoint that heat resistance and oil resistance of the obtained thermoplastic polymer composition are excellent, and a molding process is easy, the fluorine-containing ethylenic polymer (a) is preferably polyvinylidene fluoride.

【0036】

A non-fluorine-containing cured rubber (B) is at least one kind of rubber (b) which is at least partially crosslinked, and does not contain a fluorine atom in the cured rubber. Also, a non-fluorine-containing non-silicone rubber is preferable. Herein, the non-fluorine-containing non-silicone rubber is at least one kind of rubber (b) which is at least partially crosslinked, and does not contain a fluorine atom and a silicone structure comprising a silicon atom and an oxygen atom in a cured rubber.

【0037】

The rubber (b) is not particularly limited but, for example, it is preferably at least one kind of rubber selected from the group consisting of an olefin rubber, an acrylic rubber, a nitrile rubber, a silicone rubber, a urethane rubber and an epichlorohydrin rubber from the viewpoint that heat resistance and oil resistance of the obtained thermoplastic polymer composition are excellent.

【0038】

Examples of an olefin rubber are diene rubber, butyl rubber, and ethylene rubber.

【0039】

Examples of the diene rubber are natural rubber, isoprene rubber, butadiene rubber, chloroprene rubber, styrene-diene rubbers

such as a styrene-butadiene rubber and a styrene-diene-styrene block copolymer. Herein, the styrene-diene rubbers include hydrogenated articles thereof or acid modified articles thereof.

【0040】

Examples of the butyl rubber are butyl rubber, and halogenated butyl rubbers such as a chlorinated butyl rubber or a brominated butyl rubber.

【0041】

Examples of the ethylene rubber are an ethylene-propylene rubber (EPM), an ethylene-propylene-diene rubber (EPDM), chlorinated polyethylene and chlorosulfonated polyethylene.

【0042】

Examples of the acrylic rubber are acrylic rubber and ethylene acrylic rubber, examples of the nitrile rubber are an acrylonitrile-butadiene rubber and a hydrogenated acrylonitrile-butadiene rubber, examples of the silicone rubber are a dimethylsilicone rubber, a vinylmethylsilicone rubber, a phenylmethylsilicone rubber, a phenylvinylmethylsilicone rubber and a fluorosilicone rubber, and examples of the urethane rubber are a polyester urethane rubber and a polyether urethane rubber.

【0043】

Among these, from the viewpoint that heat resistance and oil resistance of the obtained thermoplastic polymer composition are excellent, it is preferable that the rubber (b) is at least one selected from the group consisting of an ethylene-propylene-diene rubber, an ethylene-propylene rubber, a butyl rubber, a halogenated butyl rubber, an acrylonitrile-butadiene rubber, a hydrogenated

acrylonitrile-butadiene rubber, a dimethylsilicone rubber, a vinylmethylsilicone rubber and a styrene-butadiene-styrene block copolymer.

【0044】

A cured rubber (B) is required to be at least partially crosslinked.

【0045】

An amount of the rubber (b) is preferably 10 to 1,000 parts by weight based on 100 parts by weight of the fluororesin (A), more preferably 50 to 900 parts by weight, and further more preferably 100 to 800 parts by weight.

【0046】

When an amount of the rubber (b) is less than 10 parts by weight, the obtained thermoplastic polymer composition tends to lower in flexibility, and when it exceeds 1,000 parts by weight, the obtained thermoplastic polymer composition tends to lower in mold-processability.

【0047】

The thermoplastic polymer composition of the present invention is obtained preferably by a preparation process in which the rubber (b) is dynamically vulcanized in the presence of the fluororesin (A) and the crosslinking agent (C) under melting conditions. Herein, being dynamically vulcanized means that the rubber (b) is dynamically vulcanized at the same time of melt-kneading by using a Banbury mixer, a pressure kneader, an extruder, etc. Among them, extruders such as a twin-screw extruder are preferable from the viewpoint of applying high shearing force. By treating with dynamic vulcanization,

there can be controlled the phase structure of the fluororesin (A) and the cured rubber (B), and dispersion of the cured rubber.

【0048】

The crosslinking agent (C) is preferably at least one selected from the group consisting of organic peroxide, an amine compound, a hydroxyl compound, a phenol resin compound, a sulfur compound, a bismaleimide compound, and a quinoid compound.

【0049】

Examples of the organic peroxide are dialkyl peroxide such as 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane and dicumyl peroxide; and hydroperoxide such as diisopropylbenzene hydroperoxide and cumene hydroperoxide.

【0050】

Also, examples of the amine compound are 6-aminohexylcarbamic acid ($H_2N-CO_2(CH_2)_6NH_2$), 1,4-butanediamine and 1,4-diaminocyclohexane.

【0051】

Also, according to the necessity, together with the crosslinking agent (C), a crosslinking aid may be used.

【0052】

The crosslinking agent (C) can be suitably selected according to kind of the rubber (b) to be crosslinked and melt-kneading conditions.

【0053】

Further, the rubber (b) preferably has at least one crosslinkable functional group in its molecule, and in this case, it is

preferable to use, as the crosslinking agent (C), a compound having two or more functional groups and being capable of reacting with the crosslinkable functional group.

【0054】

Examples of the crosslinkable functional group that the rubber (b) can contain are a hydroxyl group, an epoxy group, an amino group, a carboxyl group, an anhydrous carboxyl group, chlorine, and bromine.

【0055】

Further, for example, when a crosslinkable functional group that the rubber (b) can contain is an anhydrous carboxyl group, an amino compound can be used as the crosslinking agent (C), and when a crosslinkable functional group that the rubber (b) can contain is a hydroxyl group, an isocyanate compound or a compound containing an anhydrous carboxyl group can be used as the crosslinking agent (C).

【0056】

An amount of the crosslinking agent (C) is preferably 0.1 to 10 parts by weight based on 100 parts by weight of the rubber (b), and more preferably 0.2 to 8 parts by weight. When the amount of crosslinking agent (C) is less than 0.1 parts by weight, crosslinking of the rubber (b) cannot sufficiently proceed, and the obtained thermoplastic polymer composition tends to lower in heat resistance and oil resistance, and when it exceeds 10 parts by weight, the obtained thermoplastic polymer composition tends to lower in mold-processability.

【0057】

The melting conditions means a temperature at which the fluororesin (A) and the rubber (b) melt. The melting temperature is different depending on a glass transition temperature and/or a melting point of the fluororesin (A) and the rubber (b), and is preferably 120 to 330°C, more preferably 130 to 320°C. When the temperature is less than 120°C, dispersion between the fluororesin (A) and the rubber (b) tends to become coarse, and when more than 330°C, the rubber (b) tends to be thermally deteriorated.

【0058】

The obtained thermoplastic polymer composition may have a structure wherein the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase, or a structure wherein the fluororesin (A) and the cured rubber (B) form a mutually-continuous phase, among them, it is preferable that the composition has a structure wherein the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase.

【0059】

The rubber (b) that has formed a matrix in an initial stage of dispersion, along with proceeding of a crosslinking reaction, the rubber (b) becomes the cured rubber (B) to increase melt viscosity, so that the cured rubber (B) becomes a dispersion phase, or it forms a mutually-continuous phase with the fluororesin (A).

【0060】

Once such a structure is formed, the thermoplastic polymer composition of the present invention exhibits excellent heat resistance and oil resistance, and also has satisfactory mold-processability. On the occasion, an average dispersion particle

diameter of the cured rubber (B) is preferably 0.01 to 20 μm, more preferably 0.1 to 10 μm.

【0061】

Also, the thermoplastic polymer composition of the present invention may contain a mutually-continuous phase of the fluororesin (A) and the cured rubber (B) in the part of the structure wherein the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase, which is its preferable embodiment.

【0062】

Also, to the thermoplastic polymer composition of the present invention, the following additives such as other polymers such as polyethylene, polypropylene, polyamide, polyester and polyurethane; inorganic fillers such as calcium carbonate, talc, clay, titanium oxide, carbon black and barium sulfate; a pigment, a flame retardant a lubricant, a photostabilizer, a weather resistance stabilizer, an antistatic agent, an ultraviolet absorber, an antioxidant, a mold-release agent, a foaming agent, a perfume, an oil and a softener can be added within a range where the effect of the present invention is not affected.

【0063】

The thermoplastic polymer composition of the present invention can be processed by using general molding processes and molding process equipment. As a molding process, arbitrary processes, for example, injection molding, extrusion molding, compression molding, blow molding, calendar forming and vacuum molding can be adopted, and the thermoplastic polymer composition of the present invention can be formed into a molded article having an arbitrary shape according to intended uses.

【0064】

Further, the present invention includes molded articles of sheets or films obtained by using the thermoplastic polymer composition of the present invention, and also a laminate, which has layers comprising the thermoplastic polymer composition of the present invention and layers comprising other materials.

【0065】

The thermoplastic polymer composition of the prevent invention and the molded article, sheet and film comprising the composition can be used for automobile parts, mechanical parts, electric and electronic parts, OA parts, daily products, building materials and miscellaneous goods, and the laminate can be used for food containers, fuel containers, tubes, hoses and the like.

[Example]

【0066】

The present invention is explained in detail based on Examples in the following, but the invention is not to be limited only thereto.

【0067】

<Hardness>

Pellets of thermoplastic polymer compositions produced in Examples or Comparative Examples were compression-molded by a heat pressing machine under the conditions of 250°C and 10 MPa to prepare a sheet test piece having 2 mm thickness, of which hardness A was measured according to JIS-K6301.

【0068】

<Tensile strength at break and tensile elongation at break>

Pellets of thermoplastic polymer compositions produced in Examples or Comparative Examples were compression-molded by a heat pressing machine under the conditions of 250°C and 10 MPa to prepare a sheet test piece having 2 mm thickness, therefrom a dumbbell test piece having 2 mm thickness and 5 mm width was punched out. By using the obtained dumbbell test piece, tensile strength at break and tensile elongation at break at 23°C, and tensile strength at break at 140°C were measured with an autograph (manufactured by Shimadzu Corporation) according to JIS-K6301 at 50 mm/min.

【0069】

<Compression set>

A molded article of a right circular cylinder having a diameter of 29.0 mm and a thickness of 12.7 mm was prepared from pellets of thermoplastic polymer compositions produced in Examples or Comparative Examples by an injection molding machine at a cylinder temperature of 250°C, and according to JIS-K6301, the compression set was measured after the article was left stood under the conditions of a temperature at 120°C and 25 % of compression deformation-amount for 22 hours.

【0070】

<Chemical resistance>

Pellets of thermoplastic polymer compositions produced in Examples or Comparative Examples were compression-molded by a heat pressing machine under the conditions of 250°C and 10 MPa to produce a sheet test piece having 2 mm thickness, therefrom a dumbbell test piece having 2 mm thickness and 5 mm width was

punched out. The obtained dumbbell test piece was immersed in JIS No. 3 oil, and left stood at 100°C for 70 hours. Then, the dumbbell test piece was taken out, tensile strength at break at 23°C was measured by using an autograph (manufactured by Shimadzu Corporation) according to JIS-K6301 under the conditions of 50 mm/min, and the change ratio of the measurement to the tensile strength at break before the immersion was calculated.

【0071】

In Examples and Comparative Examples, the following fluorine-containing ethylenic polymer (a), rubber (b-1), rubber (b-2), crosslinking agent (C-1) and crosslinking agent (C-2) were used.

【0072】

<Fluorine-containing ethylenic polymer (a)>

Tetrafluoroethylene-ethylene copolymer (melting point of 220°C: "Neoflon ETFE EP-620" available from Daikin Industries, Ltd.)

【0073】

<Rubber (b-1)>

Maleic anhydride-modified product of a hydrogenated styrene-butadiene-styrene block copolymer ("Toughtec M1943" available from Asahi Kasei Corporation)

【0074】

<Rubber (b-2)>

Ethylene-propylene rubber ("EP57P", available from JSR Corporation)

【0075】

<Crosslinking agent (C-1) >

6-aminohexylcarbamic acid ("V-1" available from Daikin

Industries, Ltd.)

【0076】

<Crosslinking agent (C-2) >

2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3 ("Perhexyne 25B" available from NOF Corporation)

【0077】

EXAMPLES 1 to 3

The above-described fluorine-containing ethylenic polymer (a), rubber (b-1) and crosslinking agent (C-1) were pre-mixed in the ratio shown in Table 1, thereafter the mixture was supplied to a twin-screw extruder to be melt-kneaded at 250°C of cylinder temperature and at 100 rpm of a screw rotation number, and pellets of thermoplastic polymer compositions were respectively prepared.

【0078】

EXAMPLES 4 to 6

The above-described fluorine-containing ethylenic polymer (a), rubber (b-2) and crosslinking agent (C-2) were pre-mixed in the ratio shown in Table 1, thereafter, the mixture was supplied to a twin-screw extruder to be melt-kneaded at 250°C of cylinder temperature and at 100 rpm of a screw rotation number, and pellets of thermoplastic polymer compositions were respectively prepared.

【0079】

From morphology observation of the thermoplastic polymer compositions obtained in Examples 1 to 6 by a scanning electron microscope (manufactured by JEOL Ltd.), it was found that the

composition had a structure wherein the fluororesin (A) forms a continuous phase and the cured rubber (B) forms a dispersion phase.

【0080】

Measurements of hardness, tensile strength at break, tensile elongation at break and compression set and evaluations of chemical resistance were conducted by using the pellets of the obtained thermoplastic polymer composition according to the above methods. The results are shown in Table 1.

【0081】

COMPARATIVE EXAMPLE 1

Pellets of a thermoplastic polymer composition were produced in the same manner as in Example 3 except that the crosslinking agent (C-1) was not compounded.

【0082】

COMPARATIVE EXAMPLE 2

Pellets of a thermoplastic polymer composition were produced in the same manner as in Example 6 except that the crosslinking agent (C-2) was not compounded.

【0083】

From morphology observation of the thermoplastic polymer composition obtained in Comparative Example 1 or 2 by a scanning electron microscope (manufactured by JEOL Ltd.), it was found that the composition had a structure wherein the rubber (b) forms a continuous phase and the fluororesin (A) forms a dispersion phase.

【0084】

Measurements of hardness, tensile strength at break, tensile elongation at break and compression set, and evaluation of chemical resistance were conducted by using the pellets of the obtained thermoplastic polymer composition according to the above methods. The results are shown in Table 1.

【0085】

COMPARATIVE EXAMPLE 3

30 parts by weight of polypropylene (J106W available from Grand Polymer Co. Ltd.), 70 parts by weight of ethylene-propylene-diene rubber (EPDM EP21 available from JSR Corporation.) and 0.5 parts by weight of a crosslinking agent (PERCUMYL D available from NOF Corporation) were pre-mixed, thereafter, the mixture was melt-kneaded by a Plastomil kneading equipment under the conditions at 230°C and at 50 rpm for 10 minutes to synthesize a dynamically-vulcanized rubber (TPV-1) comprising polypropylene and crosslinked EPDM.

【0086】

From a morphology observation of the obtained thermoplastic polymer composition by a scanning electron microscope (manufactured by JEOL Ltd.), it was found that the composition had a structure wherein propylene forms a continuous phase and crosslinked ethylene-propylene-diene rubber forms a dispersion phase.

【0087】

The measurements of hardness, tensile strength at break, tensile elongation at break and compression set, and the evaluation of chemical resistance were conducted by using the pellets of only the

obtained dynamically-vulcanized rubber (TPV-1) according to the above methods. The results are shown in Table 1.

【0088】

TABLE 1

	Ex.						Com. Ex.		
	1	2	3	4	5	6	1	2	3
Amounts (part by weight)									
Fluorine-containing ethylenic polymer (a)	50	40	30	50	40	30	30	30	
Rubber (b-1)	50	60	70				70		
Rubber (b-2)				50	60	70		70	
Crosslinking agent (C-1)	0.12	0.15	0.20						
Crosslinking agent (C-2)				0.10	0.12	0.14			
Dynamically-vulcanized rubber (TPV-1)									100
Evaluation results									
Hardness	99	92	84	90	85	78	79	73	78
Tensile strength at break (MPa) at 23°C	19	15	12	20	14	12	7	9	10
Tensile elongation at break (%) at 23°C	93	125	140	102	137	156	255	234	155
Tensile strength at break (MPa) at 140°C	12	10	8	13	10	8	0	6	3
Compression set (%)	67	54	45	53	46	37	100	40	48
Chemical resistance (%)	68	51	38	73	60	47	0	29	3

[Document Name] ABSTRACT

[Abstract]

[Problem] The invention provides a thermoplastic polymer composition which has both excellent heat resistance and chemical resistance, and also has flexibility and excellent processability. [Means to solve] The present invention is a thermoplastic polymer composition comprising a fluororesin (A) and non-fluorine-containing cured rubber (B), wherein the fluororesin (A) comprises a fluorine-containing ethylenic polymer (a) with a melting point of 120 to 310°C, and the non-fluorine-containing cured rubber (B) is at least one kind of rubber (b) which is at least partially crosslinked.

[Selected Figure] None